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NQR and X-Ray Study of Bis(4-methylpyridinium) Pentabromoantimonate(III), $(4\text{-}CH_3C_5H_4NH)_2SbBr_5$

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The crystal structure of the title compound was determined (T=300 K): C_i^1-$P\bar{1}$, Z=2, a=1085.8, b=1064.3, c=929.0 pm, α=97.83, β=108.86, γ=99.24°, $R(F)$=0.047, $R_w(F)$=0.041. Characteristic for the structure is the dimer structure of $SbBr_5^{2-}$ ion. The atomic coordination around the Sb atom is a distorted octahedron. The ^{81}Br NQR spectrum was studied in the temperature range $77 \leq T/K \leq 350$. The ^{81}Br NQR frequencies are spread out over a wide range at 77 K: $37 \leq \nu(^{81}Br)/MHz \leq 111$. The temperature dependence of the NQR frequencies and of their spread is given as is an assignment of ^{81}Br NQR lines to the positions of Br atoms in the anion.

In chloroantimonates(III), Lipka observed a correlation between the bond lengths of Sb–Cl bonds trans to each other around the octahedrally coordinated Sb atoms.[1] Some time ago, Schustrovich and Buslaev suggested that in the compound AXL_m (A=main group element, X, L=ligand), in which the central atom preserves the ns^2 lone pair electrons as in halogenoantimonates(III), the effect of the σ-bond ligand X is trans influence.[2] Regarding the study of the mutual effect of ligands in bromoantimonates(III), we previously reported the crystal structures of 4,4′-bipyridinium pentabromoantimonate(III) and 2,2′-bipyridinium pentabromoantimonate(III), and the results of ^{81}Br and ^{121}Sb NQR.[3] In this work we report the crystal structure and the NQR results for the title compound in relation to a study of the mutual effect of ligands in bromoantimonate(III).

Experimental

Starting materials were commercial Sb_2O_3 and 4-methylpyridine. Bis(4-methylpyridinium) pentabromoantimonate(III) was prepared by mixing stoichiometric amounts of Sb_2O_3 and 4-methylpyridine in concd HBr solution; the salt crystallized therefrom as yellow thin needle crystals. The chemical analysis gave the following results. Found: C, 20.43; H, 2.38; N, 3.85%. Calcd for $C_{12}H_{16}N_2SbBr_5$: C, 20.31; H, 2.27; N, 3.95%.

X-Ray Crystallography. The unit cell parameters were obtained from least squares refinement of 52 reflections in the range $47.1° \leq 2\theta \leq 53.9°$. The absorption was taken into account empirically. Sb and Br positions were determined by direct methods. The positions of C and N were found from difference Fourier maps. The hydrogen atoms have been fixed by calculation, assuming sp^2 or sp^3 hybridization at the C and N along with a distance C–H and N–H of 108 pm. All non-hydrogen atoms were refined anisotropically by full matrix least squares refinement. For the H atoms an isotropic temperature factor U=600 pm^2 was used. All calculations were performed with programs SHELX 76 and SHELX 86.[4] During the intensity data collection, the standard reflections were checked in periods of 120 min and no significant change in intensity was observed. The measurement of the density was done with a pyknometer.

NQR Measurement. NQR measurements were made in the frequency range $25 \leq \nu/MHz \leq 120$ using a superregenerative type oscillator constructed following Herlach,[5] with some modifications. For the measurements in the range $8 \leq \nu/MHz \leq 25$, a Dean type superregenerative oscillator operated in external quench mode was used. The resonance lines were recorded by a chart recorder and a lock-in amplifier. No Sb NQR signals were observed in the range $8 \leq \nu/MHz \leq 120$. Besides the ^{81}Br NQR resonances, the ^{79}Br signals were observed, too. The signal to noise ratio, S/N for ^{81}Br NQR signals was 12 at 77 K.

Results and Discussion

Crystal Structure. In Table 1 the experimental conditions for the crystal structure determination are given together with some crystallographic data. These crystallographic data were in good agreement with the reported one by Stewart et al.[6] Table 2 lists the positional and thermal parameters. Intramolecular (intraionic) and intermolecular (interionic) distances and bond angles around the Sb atom are given in Table 3, together with a bond parameter n, discussed below.

In Fig. 1 two asymmetric units of the crystal structure are shown. The dimer which consists of two $SbBr_5^{2-}$ ions is connected by hydrogen bonds to the 4-methylpyridinium ions. The observed Sb–Br distances are over the range $263.0 \leq d/pm \leq 319.2$ including the interionic distance of Sb···Br(5). The Br coordination around the Sb atom is a distorted octahedron with Br–Sb–Br angles in the range $89.3 \leq /° \leq 92.7$. Hydrogen bonds are formed between Br and the hydrogen atom bonded to nitrogen in comparison with the sum of the van der Waals radii 305 pm:[7] d(Br(3)–H(N(2)))=252.1 pm with the angle of Sb–Br(3)–H(N(2))=93.3°, d(Br(4)–H(N(1)))=232.0 pm with the angle of Sb–Br(4)–H(N(1))=97.5°, d(Br(5)–H(N(2)))=290.6 pm with the angle of Sb–Br(5)–H(N(2))=82.2°, although the N–H lengths are fixed according to the assumed sp^2 hybridization at nitrogen atom.

NQR Spectra. Figure 2 shows the temperature

Table 1. Experimental Conditions of the Crystal Structure Determination and Crystallographic Data for Bis(4-methylpyridinium) Pentabromoantimonate(III)

Formula	$C_{12}H_{16}Br_5N_2Sb$
Formula weight	709.54
Habitus, Size/mm^3	Prism; (0.20×0.30×1.90)
Color	Yellow
Diffractometer	Stoe-Stadi-4
Wave lenght, λ/pm	71.069 (Mo $K\alpha$)
Monochromater	Graphite (002)
Temperature/K	300
Linear absorption coefficients, μ/cm^{-1}	114.8
Scan	$\omega/2\theta$
$(\sin\theta/\lambda)_{\max}$ 10^3/pm	11.369
Number of reflections measured	5405
Symmetry independent reflections	4496
Considered reflections	4038
Number of parameters	188
$F(000)$	656
$R(F)$	0.0473
$R_w(F)$	0.0413
Lattice constants a/pm	1085.8(5)
b/pm	1064.3(5)
c/pm	929.0(4)
α/°	97.83(2)
β/°	108.86(2)
γ/°	99.24(2)
Unit cell, $V/(10^6\times \mathrm{pm}^3)$	982.2(16)
Space group	C_i^1-$P\bar{1}$
Formula units/cell	2
$\rho_{(\mathrm{calcd})}/(\mathrm{Mg\,m^{-3}})$	2.398(14)
$\rho_{(\mathrm{obsd})}/(\mathrm{Mg\,m^{-3}})$	2.34

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{\mathrm{eq}}/(10^4\times \mathrm{pm}^2)^{\mathrm{a)}}$
Sb	0.6349(1)	0.6431(1)	0.4307(1)	3.1(1)
Br(1)	0.8424(1)	0.8373(1)	0.5704(1)	5.2(1)
Br(2)	0.6444(1)	0.6591(1)	0.1508(1)	4.7(1)
Br(3)	0.4705(1)	0.8174(1)	0.4057(1)	4.3(1)
Br(4)	0.8055(1)	0.4662(1)	0.4611(1)	4.0(1)
Br(5)	0.6043(1)	0.6061(1)	0.7255(1)	4.1(1)
N(1)	0.8620(8)	0.4165(7)	0.1313(10)	4.7(6)
N(2)	0.3926(8)	0.8386(7)	0.7340(10)	4.8(6)
C(1)	0.8011(10)	0.4303(9)	−0.0108(13)	4.6(8)
C(2)	0.8328(8)	0.3742(8)	−0.1310(11)	3.9(6)
C(3)	0.9323(8)	0.3032(8)	−0.1007(12)	4.0(6)
C(4)	0.9936(9)	0.2919(8)	0.0501(13)	4.7(8)
C(5)	0.9577(10)	0.3507(9)	0.1664(13)	5.2(7)
C(6)	0.9668(12)	0.2403(10)	−0.2291(15)	6.6(11)
C(7)	0.4169(9)	0.8085(8)	0.8718(12)	4.3(7)
C(8)	0.3661(8)	0.8680(8)	0.9726(12)	4.2(7)
C(9)	0.2877(10)	0.9555(8)	0.9309(13)	4.6(7)
C(10)	0.2637(10)	0.9804(9)	0.7854(14)	5.3(7)
C(11)	0.3178(11)	0.9219(10)	0.6867(13)	5.8(8)
C(12)	0.2348(12)	1.0247(10)	1.0416(16)	7.3(11)

a) $B_{\mathrm{eq}}=(4/3)\sum_i\sum_j \beta_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

dependence ($77\leq T/\mathrm{K}\leq 350$) of ^{81}Br NQR frequencies. Okuda et al. reported the frequencies at 77 and around 300 K which are in good agreement with our results shown in Table 4(a).[8] In Table 4(b) the parameters for fitting the NQR frequency-temperature curves to the power series. The large spread of the five ^{81}Br NQR frequencies, $37\leq \nu/\mathrm{MHz}\leq 111$ and the large spread of the distances Sb–Br, $263\leq d/\mathrm{pm}\leq 319$ offers an assignment of NQR lines to the bromine atoms in the $\mathrm{SbBr_5^{2-}}$ ion according to the theory of the electric field gradients which results in $\nu=f(1/d^3)$. In such a simple approach, often applied in literatures, the shortest Sb–Br bond would correspond to the highest ^{81}Br NQR frequency, the longest to the lowest frequency. In this way we assigned the Br atoms in the order of decreasing frequency.

Discussion. The bond order for the bromoantimonates was given by Hall et al.[9]

$$d(n)/\mathrm{pm} = 246 - 110\log_{10} n. \qquad (1)$$

n is the bond order and the fix points have been given in Ref. 9 as $d(n=1)=246$ pm for the shortest length in α-$\mathrm{SbBr_3}$ and $d(n=0.5)=279$ pm for the bond distance d(Sb–Br) of the regular octahedral $\mathrm{SbBr_6^{3-}}$ ion. The values of the bond orders for the title compound were

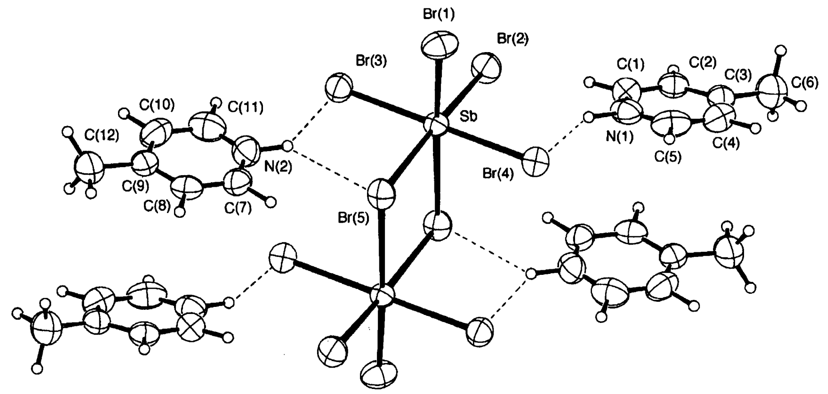

Fig. 1. The crystal structure of $[4\text{-}CH_3C_5H_4NH]_2SbBr_5$.

Table 3. Inter- and Intramolecular Bond Lengths, Bond Orders (n) of Sb–Br Bond, and Bond Angles

				Angle/°			
	d/pm	n[a)]		Br(1)	Br(2)	Br(3)	Br(4)
Sb–Br(1)[c)]	263.0(1)	0.70	Br(2)	92.7(0)			
Sb–Br(2)	266.3(1)	0.65	Br(3)	89.3(0)	90.6(0)		
Sb–Br(3)	275.6(1)	0.54	Br(4)	90.1(0)	90.1(0)	179.1(0)	
Sb–Br(4)	282.6(1)	0.46	Br(5)	92.3(0)	174.9(0)	89.5(0)	89.8(0)
Sb–Br(5)	293.4(1)	0.37					
Sb–Br(5^i)[b)]	319.2(1)	0.22					
<Sb–Br>	283.4						
Σn		2.94					
Br(3)···N(2)	340.7(9)						
Br(4)···N(1)	330.4(7)						
Br(5)···N(2)	364.7(7)						

a) The estimation of the bond order was done according to Eq. 1. b) Atoms carrying i are related to the original atoms by the relationship x, y, $z \longrightarrow 1-x$, $1-y$, $1-z$. c) The numbering for bromine atoms are in order of decreasing NQR frequency.

Table 4. (a) NQR Frequencies at 77 K and 300 K, (b) Power Series Expansion of $\nu=f(T)=\sum_i a_i \cdot T^i$ $(77<T/\mathrm{K}<350)$ for Bis(4-methylpyridinium) Pentabromoantimonate(III). Z is the Number of Experimental Points Used for the Fitting. σ is the Standard Deviation.

(a) Atom	Lines	ν/MHz (T/K=77)	ν/MHz (T/K=300)
^{81}Br	Br(1)	111.36	110.72
	Br(2)	91.72	90.39
	Br(3)	74.14	73.32
	Br(4)	61.32	59.70
	Br(5)	37.72	36.16

(b) Lines	Z	$\sigma\times10^3$/MHz	$a_{-1}10^2$/(MHz·K)	a_0/MHz	$a_1 10^3$/(MHz·K^{-1})	$a_2 10^6$/(MHz·K^{-2})
Br(1)	36	39.89	10.198	111.335	−1.265	−2.595
Br(2)	37	52.17	0.922	92.338	−8.266	5.628
Br(3)	43	39.24	1.043	75.024	−11.197	18.856
Br(4)	38	32.61	4.760	61.635	−2.397	−12.893
Br(5)	47	33.81	2.313	37.849	−0.168	−17.978

calculated by use of Eq. 1 and the sums of n for Sb–Br bonds trans to each other were nearly equal to 1.0, ranging from 0.92 to 1.02, i.e., the longer Sb–Br bond, the shorter trans Sb–Br bond. We can see the trans influence, trans weakening, of σ-bond ligands suggested by Schustrovich and Buslaev,[2)] as we reported for 4, 4′- and 2,2′-bipyridinium pentabromoantimonate(III).[3)] The title compound shows that roughly speaking, two

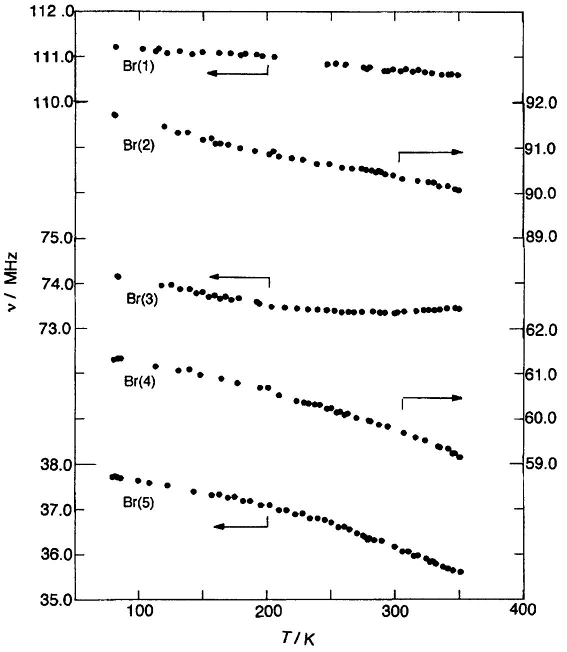

Fig. 2. The temperature dependence of ^{81}Br NQR frequencies.

pairs of ^{81}Br NQR lines, Br(3) and Br(4), Br(2) and Br(5), are symmetrically positioned to a frequency of about 66 MHz at 77 K like 4,4′-bipyridinium pentabromoantimonate, but do not show the symmetrical temperature behavior.[3] The symmetrical position of NQR lines reflects the trans influence of the σ-ligand. The frequency of 66 MHz is nearly equal to the ^{81}Br NQR frequency for the Br atom in the almost regular octahedral ion, e.g., 65.38 MHz for $[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$,[10] where each Sb–Br bond has the bond order n=0.5.

The Br(3) NQR line shows the abnormal features of the frequency-temperature curve in contrast to the feature according to the normal Bayer term,[11] i.e., the decrease of the NQR frequencies due to torsional molecular motion. It is probably due to the hydrogen bond, Br(3)–H(N(2)). The hydrogen bond will lower the NQR frequency because of the opposite contribution of the electric field gradient created by the bond $H^+\cdots Br$ and the bond Br–Sb. When the temperature increases, some thermal motion are activated and then the hydrogen bond can be broken. It results in increasing the NQR frequency. There is no phenomenon that proves the electronic rearrangement in the $SbBr_5^{2-}$ dimer followed by structural rearrangement as suggested in the case of 4,4′-bipyridinium pentabromoantimonate(III).[3]

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